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ARTICLE

Is oxidation-reduction a real robust strategy for lignin conversion? A comparative study on lignin and model compounds

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This study focuses on the oxidation-reduction method for lignin depolymerization, an increasingly popular approach to lignin valorization. The effects of oxidative pretreatment on downstream lignin hydrogenolysis were carefully studied over various heterogeneous catalysts. It was found that oxidative pretreatment provided a promising strategy to produce renewable carbonyl-containing aromatics. However, oxidative pretreatment led to decreased monomer and aromatic oil yields compared to untreated lignin using W_2C/AC and four commercial catalysts. The results with lignin contrasted with those of model compounds where the oxidative pretreatment led to increased efficiency in the cleavage of β-O-4 linkages. FT-IR, gel permeation chromatography, 2D HSQC NMR, GC-MS and elemental analysis characterization of lignin and lignin$^{\alpha\text{-OX}}$ have been used to identify possible reasons for the contrasting results found with lignin and the model compounds. It is proposed that undesired degradation of linkages, condensation and modification of lignin occurred during lignin oxidation. This work provides an advanced perspective on the oxidation-reduction strategy for lignin depolymerization.

Introduction

The growing demand for fuels and the increasing awareness of the depletion of fossil energy have driven researchers all over the world to find renewable and sustainable alternatives. Biomass is a storage form of carbon and solar energy and has attracted great interest for the potential as a sustainable resource of chemicals and fuels. Lignin accounts for 25-35% of renewable carbon in biomass and is by far the most abundant renewable source composed of aromatic units in nature.[1] Lignin depolymerization therefore becomes the key issue for its use in obtaining lignin monomers. These aromatic monomers can be further upgraded to commercial valuable aromatic chemicals such as phenol over combination of noble metal and zeolite in a fix-bed reactor, which have been developed by several groups.[2] In the past few years, various strategies such as hydrogenolysis, oxidation, photocatalysis and electrochemistry have been explored to achieve lignin depolymerization.[3] Recently, a two-step strategy combining oxidation followed by a reductive cleavage or hydrogenation reaction has been regarded as an efficient approach in lignin depolymerization.[3b, 3c, 4] This approach is justified as the oxidation of the benzylic alcohol weakens the C-O- aryl ether bond in the β-O-4 linkage, *e.g.* the bond dissociation energy (BDE) of C-O in oxidized β-O-4 units decreases to 55.9-57.0 kcal/mol compared to 68.2-71.8 kcal/mol in native β-O-4 units.[5] Therefore, it has become clear that the oxidative pretreatment of the β-O-4 linkage in a controlled manner represents an important strategy for overcoming the recalcitrance of lignin to depolymerization. Recently, several groups[4a, 4b, 6] have reported the selective oxidation of the benzylic alcohol in β-O-4 model compounds using different oxidants such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Post-oxidation, higher depolymerization activity was achieved in cleaving oxidized β-O-4 model compounds than for the corresponding unoxidized β-O-4 models in, for example, zinc-mediated approaches.[4a].

In our previous study on lignin$^{\alpha\text{-OX}}$ (product of selective lignin oxidation)[7], we found that DDQ was a useful oxidant for selective benzylic oxidation of β-O-4 units in model compounds and lignin. Further insights into the oxidation of β–β and lignin-bound Hibbert's ketone (LBHK) units were also developed. It was demonstrated that the structure of lignin$^{\alpha\text{-OX}}$ has a significant knock-on effect on the ability to produce aromatic monomers using the reported Zn/NH_4Cl reductive approach.[7] It therefore was interesting to study conversion of a well-defined lignin$^{\alpha\text{-OX}}$ into monomers using catalytic (rather than super-stoichiometric) methods. In parallel, we have recently found that activated carbon supported tungsten carbide (W_2C/AC), a platinum-like heterogeneous catalyst, exhibited promising potential for the substitution of noble metal catalysts in the selective hydrogenolysis of the major aryl ether bonds in lignin, *i.e.* β-O-4 linkages, without over-reduction of the aromatic rings.[8] Currently, the performance of W_2C/AC on oxidized model compounds or lignin$^{\alpha\text{-OX}}$ is unknown. The above two aspects of progress provided us with an opportunity to pursue the more effective transformation of lignin feedstocks to aromatic monomers through integrated strategies. In addition, current studies[3b, 3c, 4c, 9] have focused mainly on using model compounds to mimic the representative linkages in

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lignin and on comparing the dramatically increased depolymerization activity of oxidized model compounds with the unoxidized versions using a range of depolymerisation methods. However, to the best of our knowledge, such an advantage of the oxidative treatment of lignin prior to depolymerization has not yet been formally verified in the case of heterogeneous catalyst-induced depolymerization. Interestingly, Stahl and co-workers[4b] achieved more than 60 wt% yield of low-molecular-mass aromatics in the depolymerization of oxidized aspen lignin in aqueous formic acid, compared with 7.2 wt% of monomers for the unoxidized aspen lignin.

In the present study, the effect of oxidative pretreatment on the depolymerization potential of lignin and lignin$^{\alpha\text{-OX}}$ was studied over W_2C/AC and four heterogeneous catalysts. It was found that the selectivity for aromatic products was shifted from non-carbonyl-containing compounds to carbonyl-containing aromatics when lignin was replaced by lignin$^{\alpha\text{-OX}}$ as the substrate, thus providing a potential strategy for the production of renewable carbonyl-containing aromatics. On the other hand, a negative influence on lignin depolymerization was observed, *i.e.* lower monomer yields from lignin$^{\alpha\text{-OX}}$ were observed than when lignin itself was used with W_2C/AC, Ni/AC and three noble metal catalysts such as Pd/AC, Pt/AC, Rh/AC in the presence of hydrogen. This result was unexpected as it contrasted with the model compound study. The reasons behind the conflicting results were explored.

Results and Discussion

1. Hydrocracking of lignin and lignin$^{\alpha\text{-OX}}$ over heterogeneous catalysts: a comparison study.

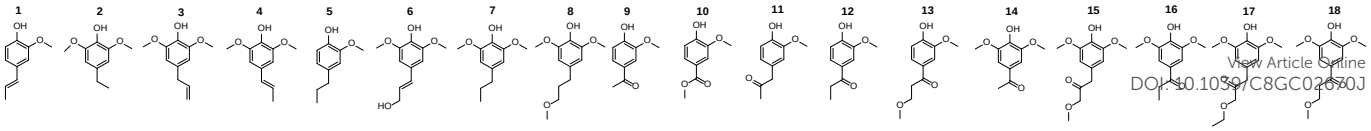
Our initial study began with the conversion of a range of hardwood lignins and the related lignin$^{\alpha\text{-OX}}$ samples to investigate the influence of the oxidative pretreatment on the depolymerization efficiency and product distribution. Previous literature[5] has reported that the BDE of the C-O aryl bond in the β-O-4 unit decreases notably after oxidation of the benzylic alcohol. It was therefore proposed that oxidative pretreatment would lead to improved depolymerization results (*e.g.* higher monomer yields with improved selectivity) than for unoxidized lignin. Dioxasolv beech lignin (BL) and oxidized BL (using 3 wt eqv. DDQ (BLO^{3WT})) were therefore prepared according to our previous method[7] and used as the substrates for depolymerization over W_2C/AC at 200 °C under 1 MPa H_2 in methanol. Brown oily products were obtained and quantified according to our previous method.[8]

As shown in **Table 1** (**Entry 1** vs **Entry 2**), the results were quite different from those expected. In terms of the yields, a much higher monomer yield of 19 wt% and total oil yield of 55 wt% (Entry 1) were observed for BL compared with yields of 12 wt% and 36 wt% for BLO^{3WT} (**Entry 2**). Given the moderate oil yield in the current system, we tried our best to improve it. Although no significant breakthrough has been achieved so far, strategies like adding capping agents (e.g., formaldehyde[10] or acetaldehyde[11]) to stabilise lignin radical have been reported recently to enhance lignin depolymerisation. Despite the product yield, further analysis of the product selectivity was explored to gain a deeper insight. It was found that BL favoured the formation of the alkyl-aromatic products originating from the hydrogenolysis of native β-O-4 unit (compounds **1**-**8**, **Scheme 1a**), while BLO^{3WT} demonstrated selectivity for carbonyl-containing aromatics that were released from oxidized β-O-4 linkages (compounds **9**-**22, Scheme 1b**). For example, compounds **1** and **7** which are typical G and S products observed on reductive depolymerisation of native lignin (**Scheme 1a**) made up 40% of the total monomers in BL oil (Entry 1), while only 3% of **1** and a trace amount of **7** were observed in the BLO^{3WT}-derived oil. Furthermore, the β-O-4 cleavage product **4** (**Scheme 1a**) constituted 49% of the total monomer yield in BL oil, but only 12% in BLO^{3WT}oil. In contrast, BLO^{3WT} revealed high selectivity for formation of **14** and **16** (17% and 14%, respectively, **Entry 2**) that originated from the β-O-4$^{\alpha\text{-OX}}$ unit (**Scheme 1b**), but neither of these two products were detected in BL oil. Overall, BL showed remarkably high selectivity (ca.100%) for aromatic monomers that did not contain a carbonyl group (**Table 1, Entry 1**); while after oxidative pretreatment, and despite the reducing conditions used in the second step, the product selectivity shifted to carbonyl-containing aromatics making up 85% of the products from BLO^{3WT} (**Table 1, Entry 2**). Taken together, on the one hand, a poorer performance was obtained from W_2C/AC-catalyzed hydrocracking of lignin$^{\alpha\text{-OX}}$ than for native lignin, *i.e.* the yields of aromatic oil and monomers were lower for BLO^{3WT} than those for BL. While on the other hand, a significant difference in product selectivity was observed between BLO^{3WT} and BL, providing the potential to tune the product distribution using an oxidation-reductive cleavage strategy.

Table 1. Catalytic hydrogenolysis of BLOs and BL over W_2C/AC.

Entry	Lignin[a]	Alkyl-aromatics selectivity[b] (%)									Carbonyl-containing aromatics selectivity[b] (%)											Yield (%)	
		1	2	3	4	5	6	7	8	Total	9	10	11	12	13	14	15	16	17	18	Total	TM (wt%)	TO (wt%)
1	BL	11	0	0	49	8	3	29	0	100	0	0	0	0	0	0	0	0	0	0	0	19	55
2	BLO^{3WT}	3	0	0	12	0	0	0	0	15	4	0	3	6	4	17	13	14	10	14	85	12	36
3	BLO$^{1.33WT}$	3	3	0	10	0	0	0	0	16	4	1	5	5	5	15	19	13	5	12	84	11	39
4	BLO$^{0.66WT}$	4	3	1	18	0	0	0	0	26	3	2	4	5	5	12	14	9	6	13	74	11	40

[a] To clarify, Beech lignin (BL), Beech lignin oxidation with 0.66 wt eqv. DDQ (BLO$^{0.66WT}$), Beech lignin oxidation with 1.33 wt eqv. DDQ (BLO$^{1.33WT}$), Beech lignin oxidation with 3 wt eqv. DDQ (BLO^{3WT}), TM = total monomers, TO = total oil. [b] Selectivity (%) = the weight of X / total monomers weight * 100%, X= Identified monomer **1**, **2**, **3-18**. *Reaction conditions*: substrate: 100 mg, 30% W_2C/AC: 100 mg, methanol: 30 mL, 200 °C, 6 h, 1 MPa H_2 (R.T.). See Figure S1 for examples of product identification by GC-MS.



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As these results were against the conclusions drawn from previous model compound studies[4b] and were beyond our initial hypothesis, two additional dioxasolv hardwood lignins, birch (BiL) and poplar lignin (PL), were prepared and were depolymerized using the above protocol. Similarly, both lignins (BiL and PL) showed higher monomer yields than the corresponding lignin$^{\alpha\text{-}OX}$ (BiLO^{3WT} and PLO^{3WT}, **Table S1**). For example, 7.4 wt% of total monomers was demonstrated in BiL oil compared to 5.8 wt% in BiLO^{3WT}oil. In PL oil, 10.2 wt% of monomers was achieved whilst 8.7 wt% was observed with PLO^{3WT} oil (**Table S1**). In addition, BiL and PL showed higher total oil yields than the corresponding oxidized lignins (BiLO^{3WT} and PLO^{3WT}, **Table S1**). Analogous differences in the product distribution were also found, namely, samples of lignin$^{\alpha\text{-}OX}$ (BiLO^{3WT} and PLO^{3WT}) resulted in carbonyl-containing aromatic as the major products while native lignins (BiL and PL) gave aromatic monomers without a carbonyl group (**Table S1)**.

To exclude any possible exceptional effects of the W_2C/AC catalyst, several commercially available catalysts with high activity towards hydrogenation including Ni/AC (20 wt% Ni loading) and three noble metal catalysts Pd/AC, Pt/AC, Rh/AC (5 wt% metal loading) were tested in the reaction under identical conditions (**Table 1**). In fact, these four catalysts exhibited even larger differences in activity for the conversion of BL and BLO^{3WT}. The depolymerisation of BL gave nearly double the monomer yields (21.2%-28.3%) compared to BLO^{3WT} (11.6%-15.3%) over all catalysts (**Figure 1 and Table S3**). As for the monomer distribution, BL afforded major products (products **1-8, Figure 1**) that were derived from unoxidized units (**Scheme 1a**) with yields ranging from 18.8% to 24.3% of the total alkyl-aromatics (**Table S3**) in all four reactions; while BLO^{3WT} showed a much broader product distribution and increased amounts of certain aldehyde or carbonyl-containing monomers (*e.g.* **16**, **18**, **Figure 1**) with 3.2%-11.2% yield of total carbonyl-containing aromatic (**Table S3**). It should be noted that selectivity for the formation of total carbonyl-containing aromatics in BLO^{3WT} was reduced over 5% Pd/AC and 5% Pt/AC compared to W_2C/AC (**Table S3**), which is most likely explained by the further reduction of carbonyl-containing aromatics (e.g., **12** and **14**) as demonstrated in **Figure S5**.

To explore possible reasons for the distinct depolymerization results between BL and BLO^{3WT}, BLOs with different extents of oxidation (BLO$^{0.66WT}$, BLO$^{1.33WT}$, BLO^{3WT}, **Table 1**) were prepared as previously reported[7] for the reaction catalyzed by W_2C/AC. It should be noted that in our previous studies BLO$^{0.66WT}$ certainly contained native β-O-4 units whilst in BLO$^{1.33WT}$ and BLO^{3WT}, most of β-O-4 units were oxidized but the degree of processing of other units varied. As shown in Entries 2-4 in **Table 1**, despite no significant differences in oil and total monomer yields (within 5%) being observed in the three BLOs, the product selectivity (*e.g.* **4, 14, 16**) was diverse. For example, 18% of the aromatic monomers was identified as **4** that was most likely generated from the cleavage of native β-O-4 units (**Scheme 1a**) in BLO$^{0.66WT}$ compared to 12% in BLO^{3WT}, implying that an increased oxidation degree of β-O-4 unit inhibited compound **4** formation. Having said that, the selectivity observed for formation of carbonyl-containing **14** (that originated from the hydrogenolysis of oxidized β-O-4, **Scheme 1b**) increased with increasing oxidation degree of β-O-4 unit. In BLO$^{0.66WT}$ oil, 12% of **14** in the total monomers was detected, while the selectivity of **14** increased to 15% and 17% in the oils of BLO$^{1.33WT}$ and BLO^{3WT}, respectively.

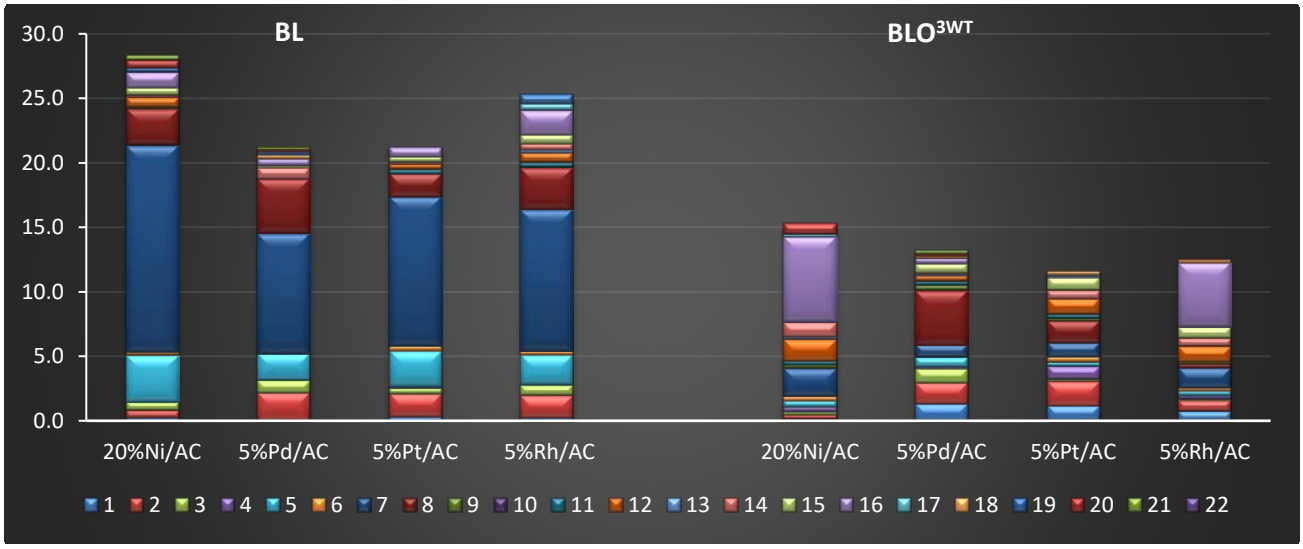

Figure 1. Depolymerization results of BL and BLOs over various catalysts.
Reaction conditions: substrate: 100 mg, catalyst: 100 mg, methanol: 30 mL, 200 °C, 6 h, 1 MPa H_2 (R.T.).

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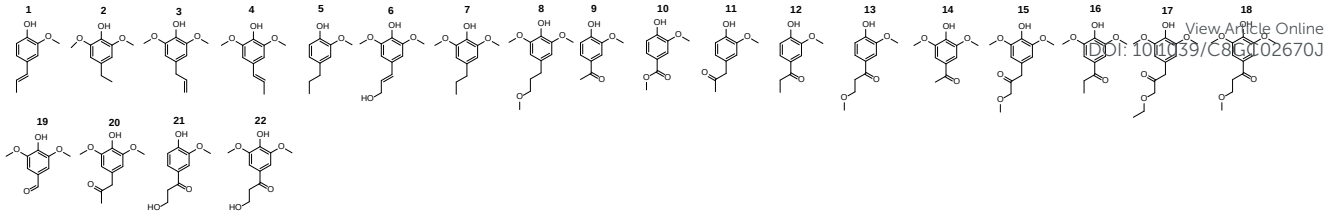
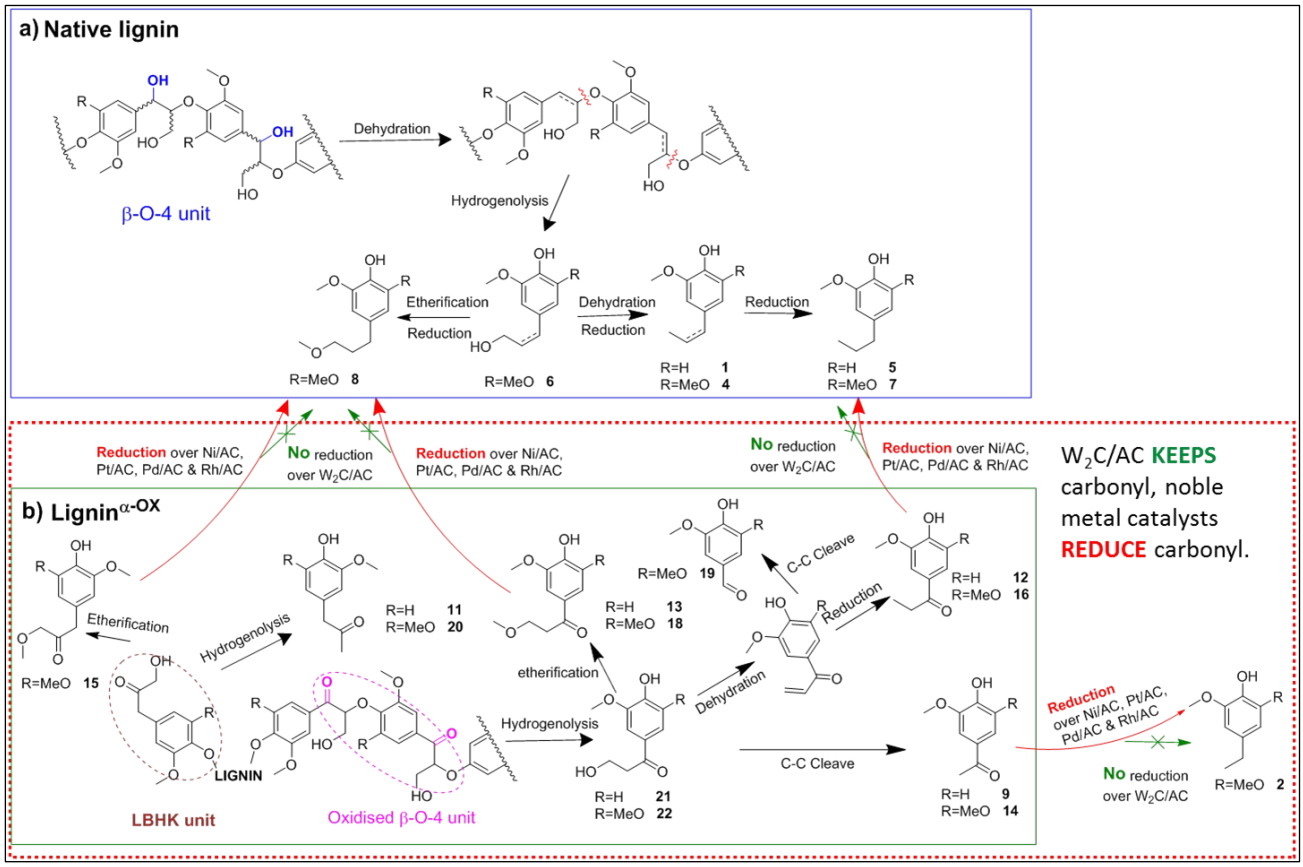


The selectivity for **16** followed the same trend as **14**, noting that **14** was also formed from the hydrogenolysis of the C-O bond in a β-O-4$^{\alpha\text{-OX}}$ unit (**Scheme 1b**). The above observations demonstrated that BLOs with a higher degree of oxidation were more likely to release products from β-O-4$^{\alpha\text{-OX}}$ units, while BL tended to generate products from native β-O-4 units.



Scheme 1. Proposed reaction mechanism for conversion of the β-O-4 unit in **a**) native lignin; **b**) lignin$^{\alpha\text{-OX}}$.

It is interesting to note that W_2C/AC kept the carbonyl functional group in lignin$^{\alpha\text{-OX}}$ depolymerization products (**Table 1** & **Figure 3** shown below), due to the moderate hydrogenation activity of W_2C/AC,[8a] while the carbonyl-containing aromatics were partially reduced to aryl-aromatics over other heterogeneous catalysts such as Ni/AC, Pt/AC, Pd/AC and Rh/AC (**Figure 1**) as shown in **Scheme 1**.

One possible rationale for lower total oil yields from lignin$^{\alpha\text{-OX}}$ (**Table 1**) is that condensation of the lignin might have occurred during the oxidative pretreatment[4a,12] as indicated by FT-IR characterization (~1330 cm^{-1}, **Figure 2**). The lower monomer yields observed in BLOs are thus reasonable. In addition, because some of the other linkages in lignin have probably been cleaved or modified during the relatively harsh oxidative pretreatment (**Table 2** & **Figure S4**), as a result, lignin$^{\alpha\text{-OX}}$ with a higher oxidation degree is more recalcitrant. It is also very interesting to note that product **14** (generated from C-C cleavage, **Scheme 1b**) showed higher selectivity in BLO^{3wt} than in the other two BLOs (i.e., BLO$^{0.66WT}$ and BLO$^{1.33WT}$), while this product was not detected in BL oil, suggesting that the BDE of C-C bonds might also be weakened after oxidative treatment of lignin. On the whole, increasing the oxidation degree through controlled oxidation[7] could shift the product selectivity from alkyl-aromatics to carbonyl-containing aromatic products, as discussed above.

Noting that lignin depolymerization via lignin$^{\alpha\text{-OX}}$ may present advantages such as enabling the use of more mild conditions,[4b] comparative experiments between BL and BLO^{3WT} at lower reaction temperatures (varying from 100 to 150 °C over W_2C/AC) were carried out. The results (**Figure 3**) confirmed that oxidative pretreatment resulted in reduced conversion efficiency. Although no obvious difference in total oil yields was observed (**Table S2**), BL showed higher total monomer yields than BLO^{3WT} under all reaction conditions (**Table S2**). In terms of the product distribution, BL provided higher selectivity towards alkyl-aromatic products (**1-8**, **Figure 2a**) compared to BLO^{3WT} which showed once more a major

distribution of carbonyl-containing aromatic products (**9-22**, **Figure 2b**).

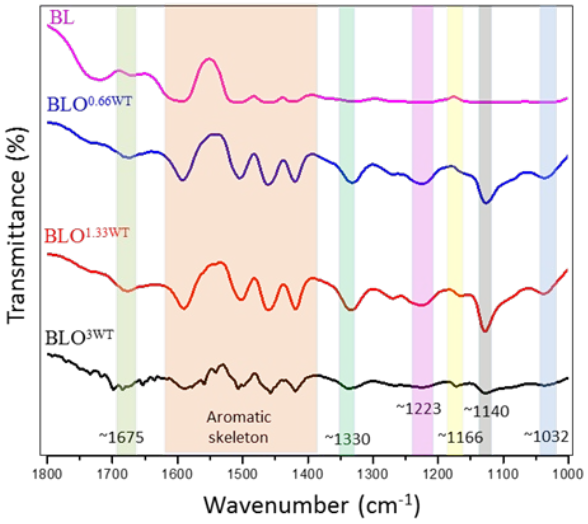


Figure 2. Zoomed FT-IR spectra of BL and BLOs. See text in ESI for more detailed discussion.

2. Oxidative pretreatment of β-O-4 model compounds.

The conflicting results between the present lignin study and the literature using model compounds triggered us to revisit the model studies. Noting that the β-O-4 linkage represents the predominant interconnecting unit in lignin,[3a] four β-O-4 model compounds (**23a-23d**) and the corresponding oxidized model compounds (**24a-24d**) were synthesized as substrates to investigate the activity of W_2C/AC for the reductive cleavage of C-O bonds under H_2 atmosphere. The only difference between **23a-23d** and **24a-24d** is in the α-position, which are a hydroxyl group and a carbonyl group, respectively. As shown in **Chart 1**, compound **23a** provided the yield of C-O bond cleavage products as low as 6% with 42% conversion (**Chart 1i**) & **Chart S2**). While after oxidative pretreatment of **23a**, the data remarkably increased to 36% and 61%, respectively for **24a** (**Chart 1ii**) & **Chart S2**), demonstrating the higher activity of **24a** than **23a** in W_2C/AC-catalyzed hydrogenolysis reaction.

Furthermore, β-O-4 model compounds with methoxy functional groups at different positions were tested. When comparing the monomer yields between **23b-23d** and the corresponding oxidized compounds **24b-24d**, similar phenomenon appeared as discussed above between **23a** and **24a**. For example, the yields of total monomers were 67%, 67% and 48%, respectively, for the conversion of **23b-23d**; comparative experiments suggested that corresponding yields increased to 100%, 100% and 88% for the conversion of **24b-24d** (**Chart 1**). These results are in accordance with literature reports[4c] that oxidized β-O-4 compounds exhibited higher yields of C-O bonds cleavage products. It is also shown in **Chart 1** that

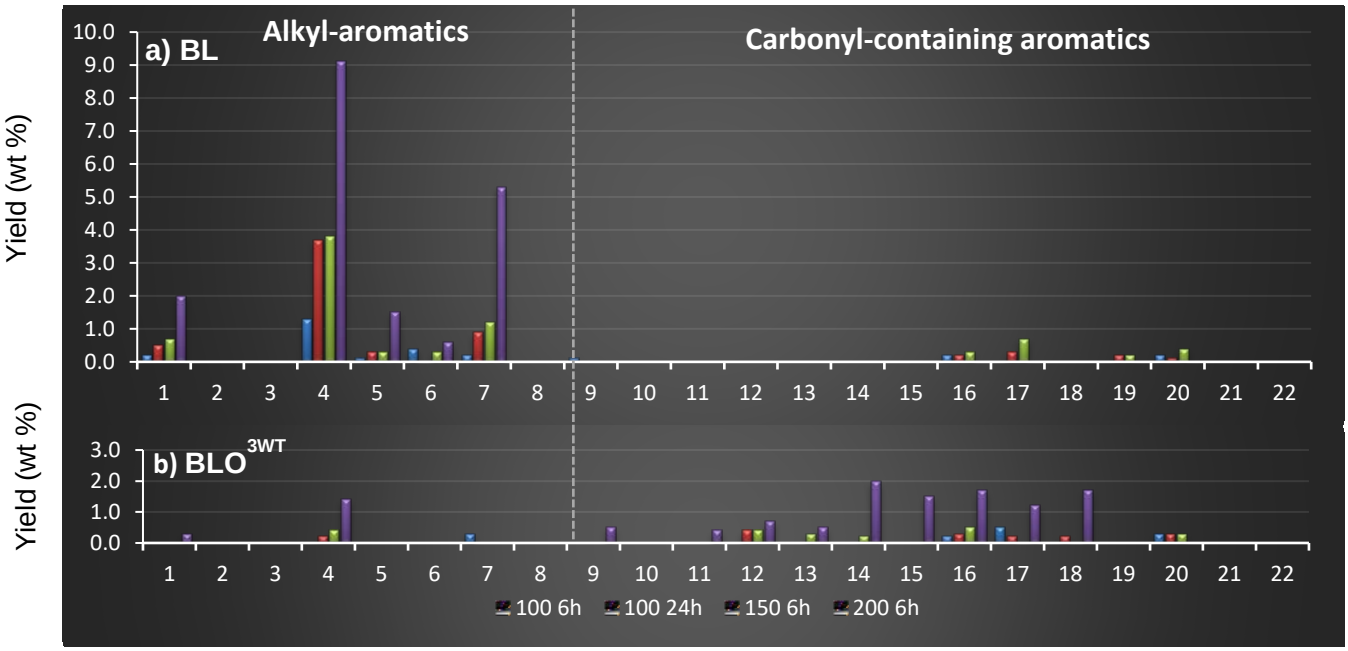
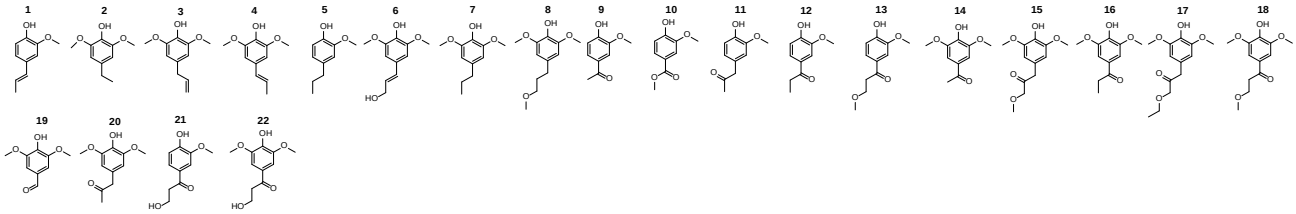


Figure 3. Further study of BL and BLO[3WT] under mild conditions over W_2C/AC.



Reaction conditions: substrate: 100 mg, 30% W_2C/AC: 100 mg, methanol: 30 mL, varied temperature, 6 or 24 h, 1 MPa H_2 (R. T.).

substrates with methoxy groups afforded higher conversion efficiency (**23a** vs **23b-23d; 24a** vs **24b-24d**), implying that the methoxy group (inductively electron-withdrawing and mesomerically electron-donating) is beneficial for the cleavage of C-Oaryl bond in the β-O-4 linkage, possibly due to the substrate having improved adsorption to the catalyst[8a, 13] or due to improved stability of a phenolic radical formed on initial homolytic cleavage of the C-Oaryl bond. Overall, the above results indicated that C-O bonds in β-O-4 model compounds containing an α-carbonyl are liable to be cleaved over W_2C/AC as compared with β-O-4 containing an α-hydroxyl group and therefore the oxidative pretreatment is desirable for the cleavage of the β-O-4 linkage in model compounds, which was in agreement with previous studies.[4c]

To look more deeply into our conflicting results between lignin and the model compounds in the present work, further characterization of the lignin$^{\alpha\text{-}OX}$ was employed. FT-IR was firstly used to understand the functional group difference between BL and the three BLOs, and the peaks were assigned according to the previous literature.[8b, 12, 14]. All the samples exhibited signals corresponding to the aromatic skeleton as discussed in **Figure S2**. Other clear differences in the functional groups between BL and BLOs were observed. As can be seen in **Figure 2**, R-C=O (~1667 cm^{-1}, light green) attributed to C=O groups conjugated with aromatic ring was observed in BLOs whilst negligible carbonyl peak was observed in BL, which was consistent with the oxidation of the benzylic alcohol in BLOs and was in accordance with the high selectivity of carbonyl-containing products from BLOs in **Table 1** and 2D HSQC NMR analysis (**Figure S6**, discussed below). Moreover, condensed S and G rings[12] (~1330 cm^{-1}, **Figure 2**) were observed in BLOs but not in BL, suggesting that condensation/repolymerization occurred during the oxidation pretreatment which would hinder the transformation of BLOs (as discussed in Section **1**). All the BLOs showed C-C/C-O/C=O signal (~1223 cm^{-1}, **Figure 2**) except for BL, and this result revealed the modification of lignin during oxidation procedure. At the same time, signal attributed to the C=O absorption conjugated with ester groups (~1166 cm^{-1}, highlighted in light yellow in **Figure 2**) was observed in BLOs, which further confirmed that new bonds might be formed during the lignin oxidative pretreatment. The presence of signals at 1140 cm^{-1} and 1032 cm^{-1} in BLOs attributed to C-O stretch of primary or trace remaining secondary alcohols (**Figure 2**) also confirmed the above hypothesis.

Furthermore, the molecular weights of BLOs and BL were analyzed by GPC to judge the impact of oxidative pretreatment on the structure of lignin. As shown in **Table 2**, BL exhibited the highest molecular weight (M_w=7809 g mol^{-1}) among all the samples, with a PDI of 3.1. While after oxidative pretreatment, the molecular weight of BLOs dropped significantly. For example, $BLO^{0.66WT}$ showed 3800 g mol^{-1} molecular weight with a PDI of 1.9, suggesting that additional linkage cleavage had occurred in $BLO^{0.66WT}$. BLOs with a higher degree of oxidation presented even lower molecular weights (*e.g.* $BLO^{1.33WT}$ M_w=3390 g mol^{-1}). BLO^{3WT} with the highest degree of oxidation degree showed the lowest molecular weight (2032 g mol^{-1}). Collectively, GPC analysis gave direct evidence of the cleavage of linkages during the lignin oxidative pretreatment and was in agreement with the hypothesis developed by FT-IR analysis.

Chart 1. Hydrogenolysis activity comparison of **i)** β-O-4 model compounds; and **ii)** Oxidized β-O-4 over W_2C/AC.

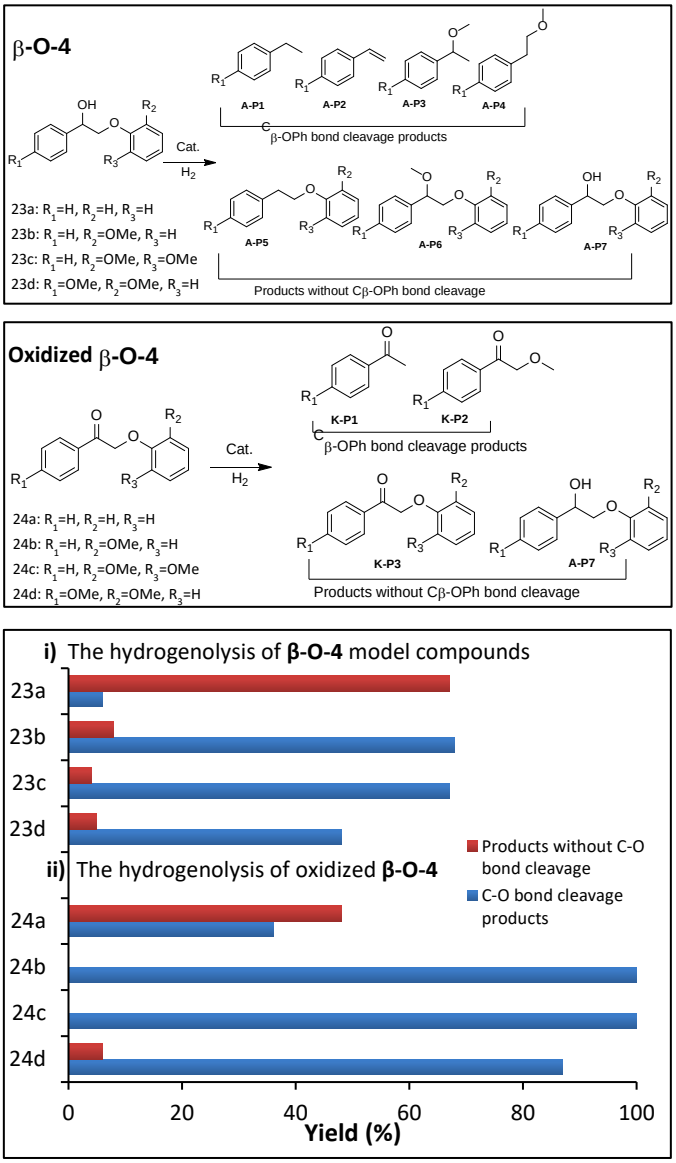


Table 2. Weighted average (Mw) and number-average (Mn) molecular weight of lignin analyzed by GPC.

Entry	Lignin	M_w (gmol^{-1})	M_n (g mol^{-1})	PDI[a]
1	BL	7809	2542	3.1
2	$BLO^{0.66WT}$	3800	2000	1.9
3	$BLO^{1.33WT}$	3390	1775	1.9
4	BLO^{3WT}	2032	1751	1.2

[a] PDI (Polydispersity)=Mw/Mn.

Our previous work has tracked the progression of various linkages (*i.e.* β-O-4, β–β and LBHK) in beech lignin during the DDQ-mediated oxidative pretreatment[7]. Therefore, we repeated the 2D-HSQC-NMR

analysis of BL and BLOs (i.e., BLO $^{0.66WT}$, BLO$^{1.33WT}$, BLO^{3WT}) and carefully revisited the NMR data to figure out the minor structure change between BL and BLOs and explain the reason why worse depolymerisation results occurred in oxidised lignin. As already known in previous study, the β-O-4 linkages (A in BL, **Figure S6**) were oxidized to carbonyl-containing linkages (A', A'' units in BLOs, **Figure S6**) with DDQ and the β-β linkage (C unit in BL, **Figure S6**) was also processed to an as yet unassigned β-β derived aldehyde (E unit in BLO^{3WT}, **Figure S6**). In addition, the fate of the β-5 unit (B in BL, **Figure S6**) was revealed in a recent studies where αβ-unsaturated phenylcoumarans were the major product during DDQ oxidation.[15] The above finding was in agreement with the FT-IR study reported here where a C=O peak was observed in BLOs. Although the evolution of β-O-4, β–β, β-5 and LBHK units, which make up nearly 80% of the linkages in hardwood lignin[3a], has been revealed during DDQ oxidation pretreatment, an unknown signal which was overlooked in the previous study[7] (i.e., red circle in BLOs in BL vs BLOs, **Figure S6**) were observed and re-evaluated . It is thought that the presence of the new unassigned cross-peaks was attributable to linkage condensation reactions during the oxidative pretreatment, which could also affect the valorization of BLOs.

Overall, it became clear that after DDQ treatment, the three main linkages (i.e., β-O-4, β-β and β-5) in lignin have been oxidized to carbonyl-containing units. As a result, higher yields of carbonyl-containing aromatics could be obtained through depolymerisation of lignins from oxidative pretreatment as discussed in Section **1**. On the other hand, such a modification could weaken C-O bonds in model compounds, and thus result in higher monomer yields in subsequent W_2C/AC catalyzed transformations as demonstrated in **Chart 1**. However, in the case of real lignin, oxidative pretreatment could not guarantee the activation of all the linkages between the primary units due to the notorious complexity of the lignin structure. It was demonstrated that oxidative pretreatment had a negative effect on the conversion performance over different heterogenous catalysts, which could be caused by the following reasons:

First, although the oxidative pretreatment lead to reduced BDE of C-Oaryl bonds due to the transformation of the α-OH to a carbonyl group, concurrent condensation (evidenced by the aforementioned FT-IR and 2D HSQC NMR characterization) may likely have occurred in lignin, which could deactivate catalytic activity of heterogeneous catalysts acting on the lignin$^{\alpha\text{-}OX}$. Second, other unknown modifications on the linkages (i.e., unassigned unit F in **Figure S6**) might also affect the valorization of BLOs. Third, as discussed above, the molecular weight decreased significantly in forming the BLOs compared with BL according to GPC analysis. It can be proposed that weaker inter-unit bonds were degraded during the oxidative pretreatment, leaving lignin$^{\alpha\text{-}OX}$ with more unreactive linkages (e.g., condensed units). On the other hand, lignin without oxidative pretreatment contains a higher fraction of reactive linkages, leading to higher yields of both monomers and total oil. The degradation hypothesis during the oxidative pretreatment was confirmed by GC-MS analysis of the liquid from the oxidative pretreatment (after lignin$^{\alpha\text{-}OX}$ had been collected by precipitation in an organic solvent, the supernatant organic solvent was concentrated *in vacuo* and analyzed, **Figure S4**). This analysis showed that new aromatic monomers (*i.e.* 1-(4-hydroxy-3,5-dimethoxyphenyl) ethan-1-one, 4-(hydroxymethyl)-2,6-dimethoxyphenol and some other unidentified low molecular weight compounds, **Figure S4**) were observed in this mixture besides solvent and DDQ-derived compounds.

Conclusions

In conclusion, the oxidation-reduction depolymerization approach for lignin provides a promising strategy to produce carbonyl-containing aromatics that could not be obtained from depolymerization of native lignin. The present work also showed that oxidative pretreatment exhibited negative effects on the yields of monomers and total oil for real lignin depolymerization over W_2C/AC, Ni/AC and three noble metal catalysts. The model compound study confirmed that improved monomers yields were obtained when oxidized β-O-4 model compounds were used over W_2C/AC. The contrasting results for lignin and the model compounds drove us to explore the reasons behind this. Structure comparison between lignin and lignin$^{\alpha\text{-}OX}$ through FT-IR, GPC, 2D HSQC NMR and GC-MS analysis suggested that whilst the oxidative pretreatment may be expected on the one hand lead to reduce the BDE of C-O aryl bonds due to the transformation of the α-OH to a carbonyl group, degradation of the linkage in the lignin, condensation and modification also occur during the lignin oxidation procedure, which would cause the lignin$^{\alpha\text{-}OX}$ structure to be more recalcitrant and hence result in the reduced monomers and total oil yields. We believe the work described here is of real importance to make researchers develop a dialectical viewpoint on the two-step strategy for renewable aromatic production.

Experimental

Materials and analytical methods: All the lignin model compounds β-hydroxy ether substrates[3f] and W_2C/AC catalyst [8a, 16]were prepared as reported in our pervious papers. All materials and chemicals were used as received unless otherwise stated. Elemental analysis was conducted on CHNS analyzer (Vario EL III, Element, Germany). All the samples were dried prior to test at 60 °C in vacuum oven. The molecular weight of all lignin samples was analyzed by gel permeation chromatograph (Viscotek TDAmax). GPC analysis was referred to the literature.[17] In a typical process, lignin sample (5 mg) was treated with pyridine (0.5 ml) and acetic anhydride (0.5 mL) for 48 h at room temperature. The mixture was concentrated in vacuo by rotary evaporation at 60 °C and washed by ethanol three times. The dried residue was filtered through syringe filter and dissolved in THF (chromatographically pure) for analysis. THF was the eluent with 1.0 mL/min flow rate at 30 °C. The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories). FT-IR was recorded on a Bruker Tensor 27 FT-IR. The signals were recorded in the range 4000-400 cm^{-1} with a resolution of 4 cm^{-1} on a spectrophotometer. KBr disc containing finely ground sample was used for analysis. 2D-HSQC spectra were perofrmed on a Bruker AVAVCE III HD 700 MHz spectrometer at 25 °C with 50 mg lignin in 0.6 mL d_6-DMSO. HSQC cross-signals were analyzed and assigned through previously published literature.[7, 18]

Lignin dioxasolv extraction: The detailed procedure was described previous.[7] In detail, to beech sawdust (70 g) was added 1,4-dioxane (504 mL) followed by 2 mol L^{-1} HCl (56 mL), and the mixture was heated with reflux at 100 °C for 1 h. The mixture was then cooled, and the lignin-containing liquor was collected by filtration. The collected liquor was concentrated in *vacuo* to give a gummy residue, and the residue was redissolved in 5mL acetone/H_2O (9:1) and then precipitated into H_2O (> 10 volumes) and stirred vigorously. The crude lignin was filtered and dried under vacuum for overnight. The dried crude lignin was dissolved in 5mL acetone/methanol (9:1) and precipitated into diethyl ether (> 10 volumes) by dropwise addition. The precipitated lignin was collected by filtration and dried in a vacuum oven to yield purified beech lignin. This lignin was used in subsequent experiments without further process.

Model compounds conversion procedure: The conversion of lignin model compound was carried out in a stainless-steel autoclave (50 mL) with an initial H_2 pressure of 1MPa and 220 °C for 2 h. Typically, lignin model compound (100 mg), catalyst (100 mg), and methanol (30 mL) were charged in a stainless-steel autoclave (50 mL), the autoclave was then charged with 1 MPa H_2 pressure of and stirred (800 rpm) at 220 °C for 2 h. Post- reaction, the reaction mixture was filtered after cooling to room temperature. The liquid phase was analyzed by GC-FID (HP-5 column, 30 m × 0.32 mm × 0.25 μm) and was quantified by internal standard (mesitylene) method.

Lignin feedstocks depolymerization procedure: The conversion of real lignin was conducted in a stainless-steel autoclave (50 mL) with 1 MPa H_2 pressure. In detail, lignin (100 mg), catalyst (100 mg), and methanol (30 mL) were added to the autoclave and stirred at 800 rpm at 200 °C for 6 h. After the reaction, the reaction mixture cooled to room temperature and was filtered. The filtrate was concentrated in *vacuo* at 45 °C to obtain liquid oil and weighed. The liquid oil was then diluted to 1.5 mL methanol (with 0.2 mg/mL internal standard), the products in liquid oil were analyzed using internal standard method (internal standard: mesitylene) with a HP 5973 GC–MS (HP-5 column, 30 m × 0.32 mm × 0.25 μm) and quantified by GC-FID.

Detailed procedure for lignin oxidation: The detailed procedure was described previous.[7] To a stirring solution of lignin (1 wt. eq.) in 1,4-dioxane (100 mg/ 2.33 mL), DDQ (0.66, 1.33 or 3 wt. eq.) is added. The solution is heated to 80 °C for 2 hours, cooled to room temperature, filtered and washed with 1,4-dioxane (1 volume). The filtrate is added dropwise to Et_2O (10 volumes) and the precipitate is filtered and washed with excess Et_2O. $Lignin^{OX}$ is dried to a constant weight in a vacuum oven at 40 °C for 24 hours prior to analysis. The resulting Et_2O filter was collected and concentrated *in vacuo*, the dried residue was dissolved in methanol and analyzed by GC-FID and GC-MS.

Conflicts of interest

There are no conflicts to declare.

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